

## OXIDATION OF MULTI-COMPONENT HYDROCARBON FUELS

Eugene Luksha and Eugene Y. Weissman

General Electric Co.  
Direct Energy Conversion Operation  
West Lynn, Massachusetts 01905

### Introduction

Because of economic necessity, commercial fuels will be used in practical fuel cell devices. Commercially available fuels generally consist of complex mixtures of hydrocarbons, primarily straight and branched aliphatics, olefins, naphthenes, and aromatics. The aliphatic compounds both straight and branched-chained are relatively reactive in fuel cells, while the unsaturated and cyclic compounds are considerably more difficult to oxidize and have been designated as "unreactive." These types of compounds are believed to adsorb on an electrode surface more rapidly than aliphatic compounds, forming an inert ad-layer. For this reason, it is necessary to know the tolerance of an operating fuel cell anode to these "unreactive" compounds.

### Experimental

The model fuel taken into consideration was split into its principal components: paraffins, olefins, naphthenes, and aromatics (Figure 1). Normal octane was chosen as the base fuel and various quantities of single unreactive components were added. The additives were chosen on the basis that they are all found in relatively high concentrations in various types of hydrocarbon fuels (1-3), and have boiling points lower than 350°F, the practical upper temperature limit of the electrodes used in this work. As a result, compounds containing more than 1 ring as, for example, indanes, indenenes, tetralins, and naphthalenes were not considered since they all have boiling points in excess of 350°F. Since hydrocarbons with condensed rings were eliminated, only alkylbenzenes, 1-ring naphthenes, in addition to the olefins and paraffins were studied.

These compounds were added to n-octane in varying concentrations. Polarization curves were taken using the binary solution as a fuel. These curves were measures of the decrease in cell performance caused by the addition of the "unreactive components."

The experimental equipment has been described elsewhere (4). The following conditions apply to the present work:

- 1) The electrodes used were 3 in. x 3 in. (0.05 ft.<sup>2</sup> active geometric area) platinum - Teflon - screen composites of a type previously described (5). The platinum loading was 35 mgms/cm<sup>2</sup> and the composition: 85 wt. % Pt - 15 wt. % TFE. The current collecting screen was generally gold-plated expanded tantalum (5<sup>1</sup> Ta 10 4/0),— and sometimes wire-woven platinum (45 mesh).
- 2) The electrolyte was 95 wt. % phosphoric acid and, as mentioned above, the maximum practical operating temperature compatible with this electrode structure was found to be 350°F.
- 3) The counter-electrodes (cathodes) consisted of platinum - Teflon - platinum screen (woven, 45 mesh) composites with the same composition and loading as the anodes.
- 4) The experimental procedure for obtaining the polarization data was identical for each fuel studied. When the cell reached the desired temperature, the fuel was introduced at a flow rate of 20 μl/min. \* and the O. C. V. was allowed to stabilize for approximately 1/2 hour. The fuel flow rate was determined by observing the pressure drop across a calibrated capillary.
- 5) Prior to the start of each run, the anode potential was raised to approximately 1 volt for 30 seconds in order to activate the electrode. The current was then shut-off and the potential was allowed to stabilize. This point was recorded as the O. C. V.
- 6) A Kordesch-Marko bridge was used to control the current through the cell. To determine the initial portion of the polarization curve, small increases in the current were made in the range of 0 to 1 amp (0 to 20 ASF). At each current setting, the anode potential was allowed to stabilize, before being recorded. Above 1 amp (20 ASF) the current changes were made in steps of 1/2 amp until the anode potential reached approximately 0.6 volt. Above this potential, current increases were made in smaller steps as the limiting current was approached. The limiting current was taken as that current at which the anode potential would no longer stabilize. Following each run, the fuel was purged from the anode with nitrogen for 10 minutes. With the nitrogen purge on, the anode potential was brought up to about 1 volt to remove traces of fuel from the electrode surface.

## Results and Discussion

### A. Binary Mixtures

#### 1. Aromatic Additives

Anode performance losses for n-octane with various aromatic additives are summarized in Table 1 and Figure 2.

\* This corresponds to 10 times the theoretical requirement of octane at 30 AS

Table 1  
Anode Performance Loss for Addition of Aromatics to n-Octane

Fuel Composition, mole %	Electrode No.	Anode Performance Loss,* mv				
		0 ASF	20 ASF	30 ASF	50 ASF	70 ASF
99% n-octane + 1% benzene	3515**	15	10	13	25	—
97% n-octane + 3% benzene	3515**	30	70	95	80	—
95% n-octane + 5% benzene	3515**	40	130	155	—	—
99% n-octane + 1% toluene	1050	20	25	35	55	—
97% n-octane + 3% toluene	1050	40	60	80	—	—
95% n-octane + 5% toluene	1050	65	205	210	—	—
99% n-octane + 1% m-xylene	1054	35	30	40	45	60
97% n-octane + 3% m-xylene	1054	50	70	90	120	—
95% n-octane + 5% m-xylene	1054	50	85	115	—	—
99% n-octane + 1% 1, 2, 4-trimethylbenzene	5305	10	30	45	75	—
97% n-octane + 3% 1, 2, 4-trimethylbenzene	5305	40	130	190	—	—

\* Defined as the increase in anode potential over that measured for pure octane at the same conditions.

\*\* Gold-plated tantalum screens. The other electrodes were supported on platinum screens.

There appears to be an effect on anode performance, in terms of molecular weight and/or degree of complexity of the additive, with the heavier (more complex) additives causing higher anode overvoltages.

The effects are generally small since the concentrations of the additives are small. It is expected that differences may become more pronounced as the concentrations of the additives increase.

In spite of some scatter in the experimental data, certain trends have been observed for the change in anode performance as a function of the additive complexity. This result is indicated in Figures 3 and 4 where the anode performance is shown to decrease with an increase in the number of carbon atoms (methyl groups) on the aromatic molecule. At this time, further comments on this behavior are not warranted.

## 2. Naphthene Additives

The naphthenes that were evaluated can be divided into two classes. The six-membered ring types which, under anode operating conditions, may be dehydrogenated to aromatics, and the five-membered ring types which appear to behave like paraffins.

The anode performance loss for these fuels is shown in Table 2 and Figure 5.

It appears that cyclohexane is more harmful to anode performance than methylcyclohexane possibly because the presence of the electrophilic methyl group in the latter species would make dehydrogenation to an aromatic structure more difficult, and it is the aromatic structure that would cause the higher anode overvoltages.

Probably the most significant result in Table 2 is the high tolerance of a fuel cell anode to rather high concentrations of cyclopentyl naphthenes. This is important since a great many logistic fuels contain high concentrations of this type of compound.

## 3. Olefin Additives

The anode performance loss for various n-octane-olefin fuel mixtures is summarized in Table 3 and Figure 6. There appears to be a relationship between the type of olefin (straight-chained, branched, cyclic) and performance. The straight-chained olefins are apparently the most difficult to oxidize. The chain length of the linear olefin is of little importance to anode performance, except at high current densities, as is evident when one compares octene-1 with pentene-1. Here, at least, the detrimental effect of higher molecular weights is not apparent. The position of the double bond in the olefin molecule also plays a role in determining the anode performance penalty. As the double bond is moved toward the center of the molecule, the anode performance penalty is slightly reduced. This result can be seen by comparing octene-1 with octene-2 in Table 3.

Table 2  
Anode Performance Loss for Addition of Naphthenes at 350°F

Electrode Composition Mole %	Electrode No.	Surface Area, m <sup>2</sup> /g	Anode Performance Loss*, mv						
			0 ASF	20 ASF	30 ASF	50 ASF	70 ASF	90 ASF	i <sub>L</sub> ASF
99% n-octane + 1% cyclohexane	3497	9.42	17	20	15	20	20	40	134
97% n-octane + 3% cyclohexane	3497	9.42	27	50	52	70	80	110	119
95% n-octane + 5% cyclohexane	3497	9.42	27	60	72	110	120	210	105
99% n-octane + 1% methylcyclohexane	1052**	—	25	0	0	0	0	—	84
97% n-octane + 3% methylcyclohexane	1052**	—	55	7	23	35	50	—	75
95% n-octane + 5% methylcyclohexane	1052**	—	100	23	45	80	—	—	64
95% n-octane + 5% methylcyclopentane	1058**	—	0	0	0	0	0	0	98
90% n-octane + 10% methylcyclopentane	3576	9.65	0	0	0	0	0	0	94
85% n-octane + 15% methylcyclopentane	3576	9.65	0	0	0	0	0	0	90

\* Defined as the increase in anode potential over that measured for pure octane at the same conditions.

\*\* Electrodes supported on Pt screen.

Table 3  
Anode Performance Loss for Addition of Olefins at 350°F

Fuel Composition, mole %	No. Allylic Hydrogen Atoms	Electrode No.	Surface Area, m <sup>2</sup> /g	Anode Performance Loss, *						
				0 ASF	20 ASF	30 ASF	50 ASF	70 ASF	90 ASF	iL ASF
99% n-octane + 1% octene-1	2	1051**	—	9	0	0	0	0	30	90
97% n-octane + 3% octene-1	2	1051**	—	20	20	25	55	120	—	72
95% n-octane + 5% octene-1	2	1051**	—	50	45	75	150	—	—	53
99% n-octane + 1% octene-2	5	1059**	—	5	0	0	0	0	0	107
97% n-octane + 3% octene-2	5	1059**	—	25	15	20	20	25	20	97
95% n-octane + 5% octene-2	5	1059**	—	35	30	35	48	120	—	74
99% n-octane + 1% 2-methylbutene-2	9	3543	11.01	0	0	0	0	0	—	89
97% n-octane + 3% 2-methylbutene-2	9	3543	11.01	5	0	0	0	0	—	86
95% n-octane + 5% 2-methylbutene-2	9	3543	11.01	5	0	0	0	5	—	84
99% n-octane + 1% 2-methylbutene-1	5	3497	9.42	20	0	0	0	0	0	121
97% n-octane + 3% 2-methylbutene-1	5	3497	9.42	30	0	0	0	0	0	114
95% n-octane + 5% 2-methylbutene-1	5	3497	9.42	40	0	0	0	0	10	107
99% n-octane + 1% pentene-1		3544	10.22	10	0	0	7	20	34	110
97% n-octane + 3% pentene-1		3544	10.22	20	35	50	52	55	73	98
95% n-octane + 5% pentene-1		3544	10.22	20	35	50	52	55	98	96
99% n-octane + 1% cyclohexene		3515	—	-5	40	47	50	40	—	89
97% n-octane + 3% cyclohexene		3515	—	-10	75	80	98	115	—	75
95% n-octane + 5% cyclohexene		3515	—	-50	135	127	—	—	—	50

\* Defined as the increase in anode potential over that measured for pure octane at the same conditions.

\*\* Electrodes supported on Pt screen.

The branched olefins do not appear to cause any significant performance penalty when present in concentrations up to 5%.

All these facts may be related to the number of allylic hydrogen atoms that the olefins contain (column 2, Table 3). On a qualitative basis, given a series of hydrocarbons containing a single double bond, the olefin containing the largest number of allylic hydrogen atoms will be least harmful to anode performance. This appears to be the case here. An explanation of the phenomenon awaits further clarification.

The cyclic olefins (cyclohexane derivatives) form a separate class of compounds and exhibit higher anode overvoltages than the other types of olefins. These compounds are probably dehydrogenated under anodic conditions (see also, negative values of O.C.V. in Table 3) to aromatics, and as a result behave more like aromatics than like olefins. One point that should be emphasized is that an unsaturated six-membered ring is extremely detrimental to anode performance no matter what may be the degree of unsaturation.

#### 4. Mixtures of Normal and Branched Paraffins

Polarization curves for cells operating on fuels consisting of mixtures of normal and iso-octanes, with 25 to 75 mole % iso-octane show no change in performance as compared to pure n-octane (see Figure 7). This indicates that branched and straight-chained paraffins having the same number of carbon atoms are very similar in reactivity. This is useful result since it increases the flexibility of a choice of multi-component fuels for specific performance requirements.

#### B. Multi-Component Mixtures

The above results were for mixtures of n-octane with single "unreactive" components. Experiments were conducted in which several "unreactive" components were added to n-octane. The polarization curve of an anode operating on a fuel consisting of 89 mole % n-octane, 5 mole % methylcyclohexane, 5 mole % octene-2, and 1 mole % toluene is shown in Figure 8. The concentrations of each of the additives was determined from Figures 3, 5 and 6 so that the anode performance penalty for each of these components is roughly 50 mv at 30 ASF.

The outstanding feature of these results is that the cumulative effect of the "unreactives" does not appear to be additive. In fact, the performance loss is similar to that obtained for the corresponding binary mixtures, meaning that at these concentration levels each ingredient is independent of the others present in the mixture.

This seems to suggest that, should a multi-component mixture be chosen with any combination of ingredients, the performance penalty will be the one roughly corresponding to the "worse offender" in the mixture (as exhibited in a binary mixture with octane).

The main question, then, becomes one of establishing the influence of the other possible performance-determining parameters, such as the fuel flow rate.

### C. Anode Performance at Other Temperatures

In an effort to determine the magnitude of a performance gain that may be obtained by increasing the operating temperature, several cells containing typical "unreactive" compounds were run at 300, 350 and 400°F. The data at 300 and 400°F are given elsewhere (6), while the data obtained at 350°F are given in Tables 1 to 3.

The log of the current at anode potentials of 0.4 volt for various fuels at 300, 350 and 400°F was plotted against  $1/T$ . From the Arrhenius-type relationship shown in Figure 9 an approximate activation energy of 13 Kcal/gmole is obtained; this is indicative of a strong temperature dependence. Although the data does not form a true straight line, probably because a variety of fuels were used, the trend toward significantly increased anode performance is evident. A linear extrapolation to a cell operating temperature of 500°F, for example, indicates the possibility of obtaining about 10-fold increase in performance, assuming, of course, compatible electrode structures are available.

### Conclusions

The performance of a platinum-activated anode oxidizing binary mixture of n-octane and various small amounts (generally 1 to 5 mole %) of hydrocarbon additives in hot concentrated acid electrolytes (95%  $H_3PO_4$  at 350°F) depends on the nature of the additive. Thus:

- 1) For aromatic additives an increase in molecular weight or degree of complexity of the aromatic molecule (e. g., number of methyl groups) will determine a corresponding increase in anode overvoltage.
- 2) For naphthene additives the opposite appears to be true (when comparing methyl cyclohexane to cyclohexane). These findings are, however, in need of further experimental evidence.
- 3) For olefin additives there is a distinct relationship between the type of olefin (straight-chained, branched, or cyclic) and performance; on an overall basis, the number of allylic hydrogens in the non-cyclic additive molecule appears to set a characteristic trend, with the anode overvoltage decreasing as the number of allylic hydrogens increases.

The cyclic olefin is quite aromatic in character due to an apparent dehydrogenation mechanism preceding the oxidation step. Specifically, six-membered cyclic olefins are very harmful to the performance of the anode both on a relative basis (compared to the other types of olefins) and on an absolute basis.

- 4) Iso-paraffins (in any proportion) do not affect the performance of normal paraffins having the same number of carbon atoms.

The detrimental effects of various additives, as obtained from performance data of binary mixtures (with octane), are not cumulative. Therefore, a multi-component mixture will not necessarily contribute more to the rise of the anode overvoltage than the single "worse offender" in the mixture.



Sizeable performance gains can be made by increasing cell operating temperatures. For example, if compatible materials and electrode structures were available so that a cell could be operated at 500°F, as much as a 10-fold increase in cell performance would be possible, based on a linear extrapolation of the existing data.

#### Acknowledgement.

This work was sponsored by the U.S. Army Engineer Research and Development Laboratories, Ft. Belvoir, Virginia under contract number DA 44-009-AMC-479(T).

The authors are grateful for the able assistance of Mr. Lucien Brassard who performed much of the experimental work.

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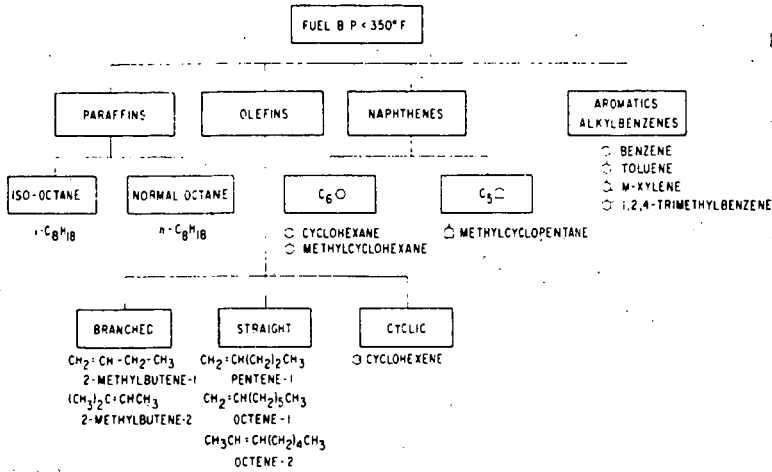


Figure 1 Principal Components of Model Fuel.

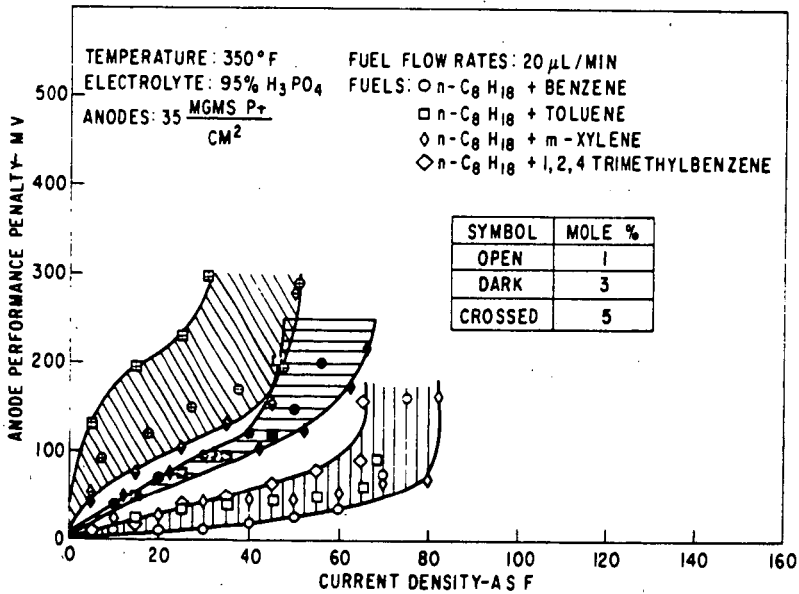


Figure 2 Anode Performance Penalty for Aromatics at 350°F.

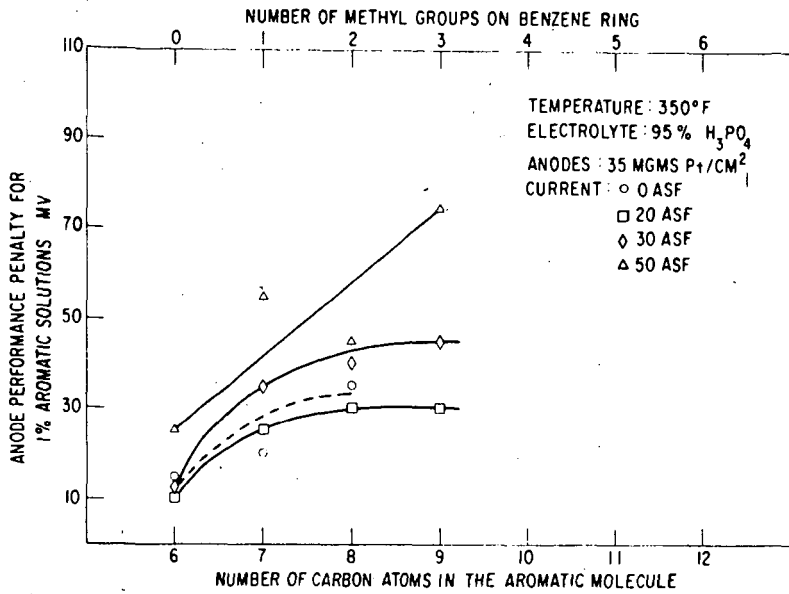


Figure 3 Anode Performance Penalty vs Number of Carbon Atoms on the Aromatic Molecule Additive.

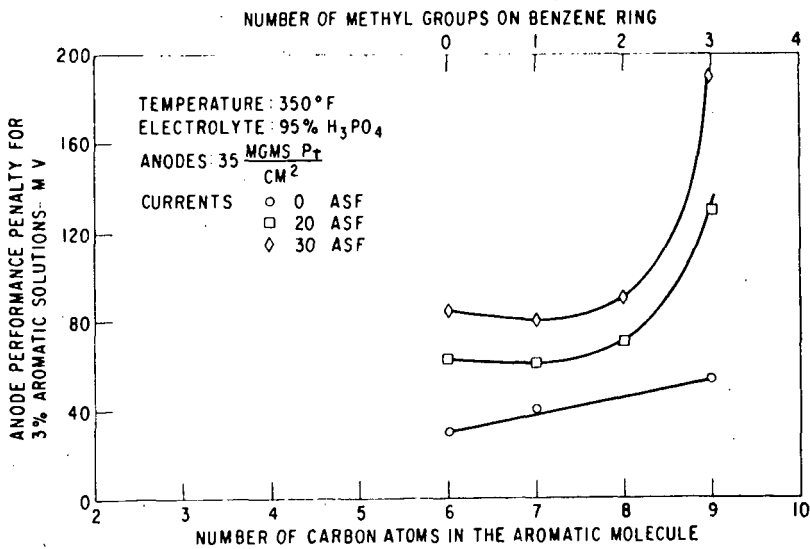


Figure 4 Anode Performance Penalty vs Number of Carbon Atoms on the Aromatic Molecule Additive.

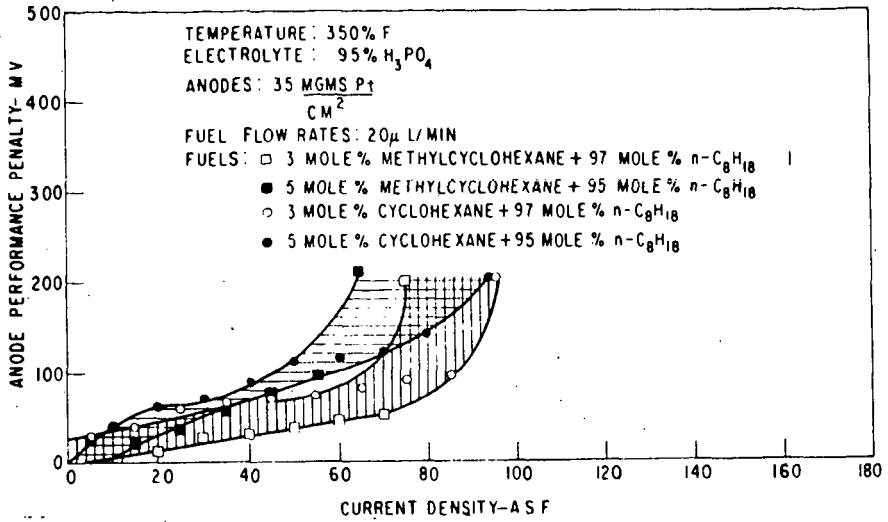


Figure 5 Anode Performance Penalty for Cyclohexyl Naphthenes at 350°F.

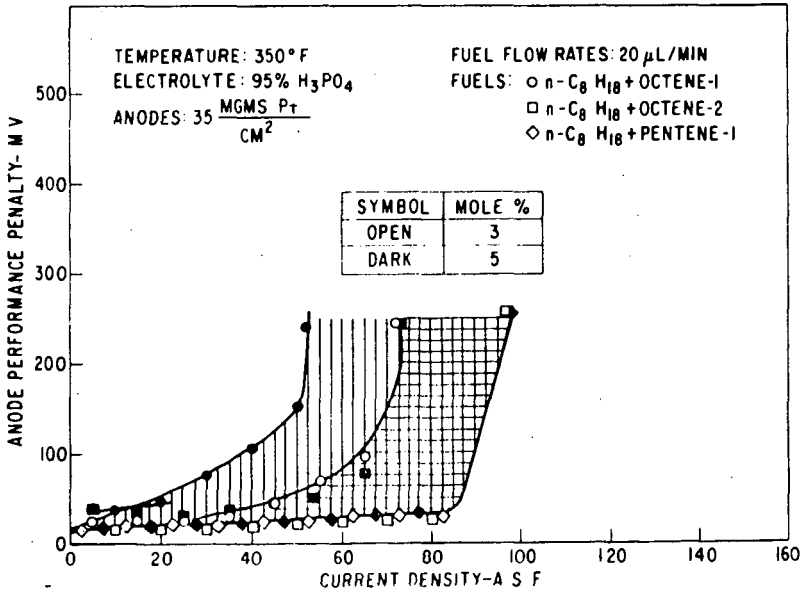


Figure 6 Anode Performance Penalty for Straight Chained Olefins at 350°F.

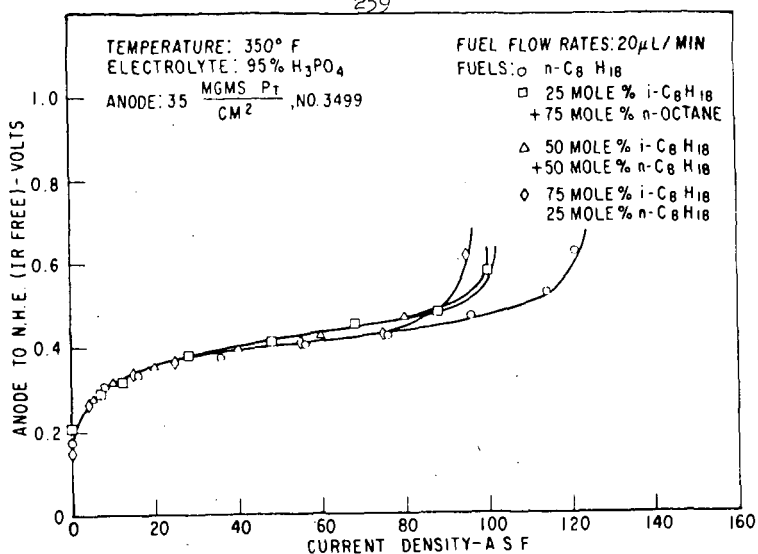


Figure 7 Anode Polarization for n-Octane and iso-Octane Mixtures at 350°F.

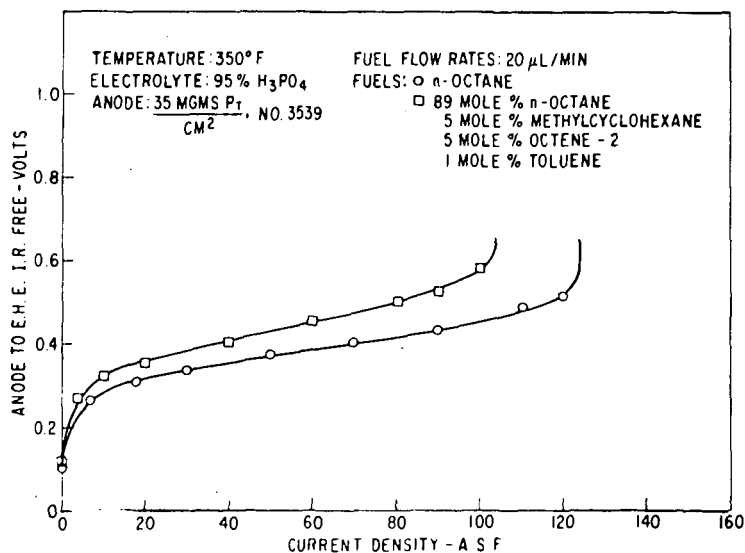


Figure 8 Anode Polarization Curve for a Fuel Mixture Consisting of 89 mole % n-Octane, 5 mole % Methylcyclohexane, 5 mole % Octene-2, and 1 mole % Toluene at 350°F.

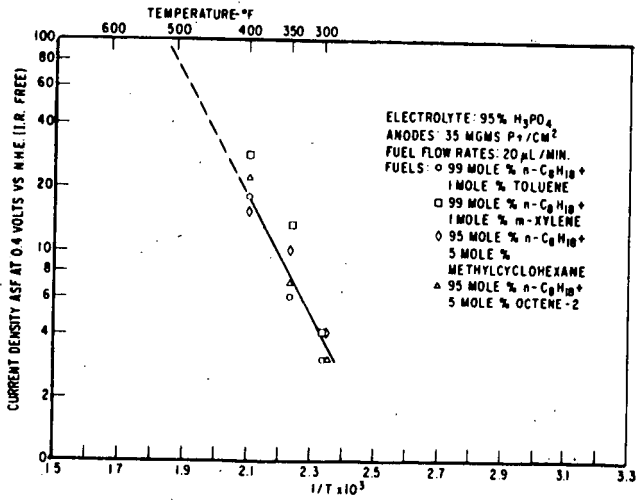


Figure 9 Current at an Anode Potential of 0.4 Volt vs  $1/T$ .